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PHENYLSULPHONEORTHOCARBONIC ACID AND RELATED COMPOUNDS.

Dissertation.

Submitted to the Board of University Studies of
the Johns Hopkins University in conformity
with the requirements for the degree
of Doctor of Philosophy.

By

HOWARD W. DOUGHTY.

1904.

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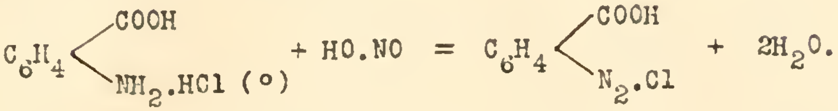
PHENYLSULPHONEORTHOCARBONIC ACID AND RELATED COMPOUNDS.

I. INTRODUCTION.

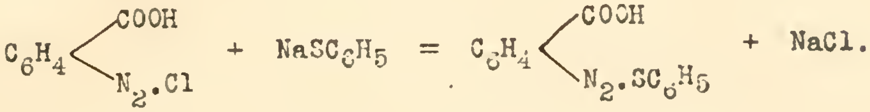
In 1890 Ziegler(1) prepared phenylthiosalicylic acid from anthranilic acid and thiophenol;

I.



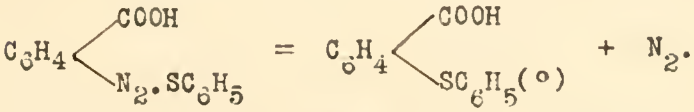
$$C_6H_4\left<\begin{array}{l}COOH\\NH_2.HCl\ (o)\end{array}\right. + HO.NO = C_6H_4\left<\begin{array}{l}COOH\\N_2.Cl\end{array}\right. + 2H_2O.$$

II.



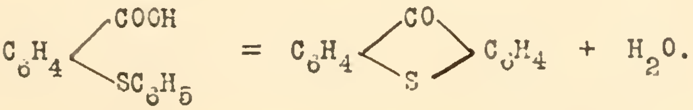
$$C_6H_4\left<\begin{array}{l}COOH\\N_2.Cl\end{array}\right. + NaSC_6H_5 = C_6H_4\left<\begin{array}{l}COOH\\N_2.SC_6H_5\end{array}\right. + NaCl.$$

III.

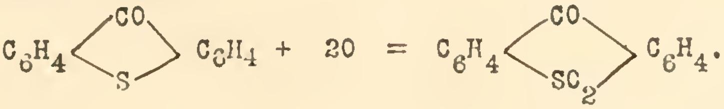


$$C_6H_4\left<\begin{array}{l}COOH\\N_2.SC_6H_5\end{array}\right. = C_6H_4\left<\begin{array}{l}COOH\\SC_6H_5(o)\end{array}\right. + N_2.$$

He did not isolate the intermediate diazo compound. By heating phenylthiosalicylic acid with concentrated sulphuric acid he obtained thioxanthone, water being eliminated:



By oxidation of thioxanthone by means of chromic acid, he obtained benzophenonesulphone:



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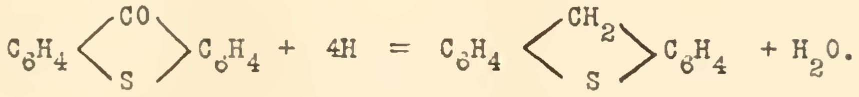
1. Ber. d. Chem. Ges. 23, 2469.

In 1891 Graebe and Schultess(1) continued the investigation of phenylthiosalicylic acid and its derivatives. They isolated the intermediate diazo ether, and then investigated the condensation product formed by heating phenylthiosalicylic acid with sulphuric acid, with the following results:

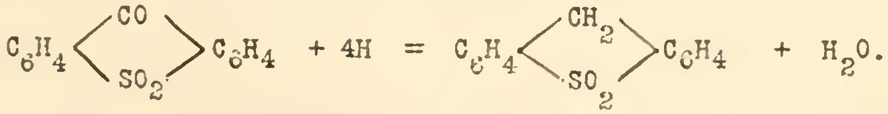
Thioxanthone, reduced by means of hydriodic acid or zinc dust, gives diphenylenemethane sulphide;



$$C_6H_4\left\langle\begin{matrix}CO\\S\end{matrix}\right\rangle C_6H_4 + 4H = C_6H_4\left\langle\begin{matrix}CH_2\\S\end{matrix}\right\rangle C_6H_4 + H_2O.$$

By oxidation of this product benzophenonesulphone is formed, the intermediate compounds not being obtained. They showed that this substance is identical with the one obtained by Beckmann,(2) who obtained it as a by product when benzophenone was subjected to the action of fuming sulphuric acid.

When benzophenonesulphone is reduced by means of hydriodic acid in the presence of red phosphorus, diphenylenemethanesulphone is formed, which is one of the two possible intermediate products between benzophenonesulphone and diphenylenemethane sulphide:



$$C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle C_6H_4 + 4H = C_6H_4\left\langle\begin{matrix}CH_2\\SO_2\end{matrix}\right\rangle C_6H_4 + H_2O.$$

Graebe and Schultess also showed that orthodiazotoluene chloride yields orthotolylphenyl sulphide when treated with sodium thiophenolate. When the vapor of orthotolylphenyl sulphide is passed through a heated tube, diphenylenemethane sulphide is formed:

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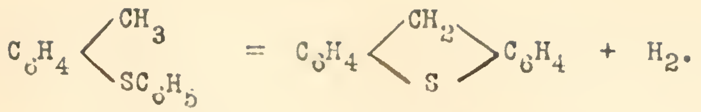
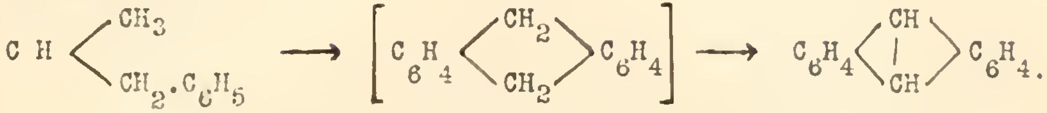
(1) Ann. Chem. (Liebig) 263, 1.

(2) Ber. d. Chem. Ges. 6, 1112; 8, 992.

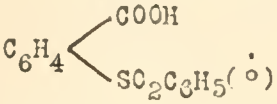


$$C_6H_4\left\langle\begin{matrix}CH_3\\SC_6H_5\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH_2\\S\end{matrix}\right\rangle C_6H_4 + H_2.$$

This reaction is analogous to the formation of anthracene from orthobenzyltoluene:



$$C\ H\left\langle\begin{matrix}CH_3\\CH_2.C_6H_5\end{matrix}\right. \longrightarrow \left[C_6H_4\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle C_6H_4\right] \longrightarrow C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4.$$

Graebe and Schultess also treated phenylthiosalicylic acid with dilute nitric acid and obtained a product to which they gave the name "sulphobenzideorthocarbonic acid" and which they considered to have the formula,  $C_6H_4\left\langle\begin{matrix}COOH\\SO_2C_6H_5(^{o})\end{matrix}\right.$.

They analysed the substance and obtained results in accord with this view. They did not describe any salts of this acid.

The corresponding acid in the para series, "paraphenylsulphonebenzoic acid", had already been made and described in 1878, by Michael and Adair,(1) who gave it this name, and who found its melting point to be over 300°. They first prepared paratolylphenylsulphone by the action of benzenesulphonic acid, toluene and phosphorus pentoxide, and also from toluenesulphonic acid, benzene and phosphorus pentoxide. They oxidized this sulphone by means of potassium permanganate in acetic acid solution, and also in water, and obtained a small yield of paraphenylsulphonebenzoic acid.

Paratolylphenylsulphone was also made in the same year, 1878, by Beckurts and R. Otto,(2) by the action of toluene and aluminium chloride on benzenesulphone chloride. In 1885 R. Otto(3) made it from toluenesulphone chloride, benzene and mercury diphenyl.

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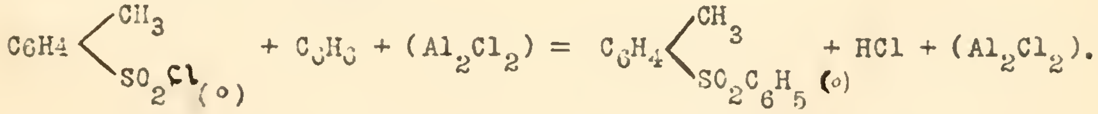
(1) Ber. d. chem. Ges. 11. 116.
(2) Ber. d. chem. Ges. 11, 2068.
(3) Ber. d. chem. Ges. 18, 249.

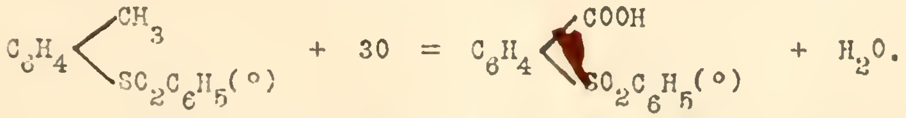
In 1895, Nowell,(1) working in this laboratory, made paraphenylsulphonebenzoic acid by oxidizing paratolylphenylsulphone, which he obtained by the action of benzene and aluminium chloride on paratoluenesulphone chloride. He found the melting point of paraphenylsulphonebenzoic acid to be 273°(uncorr.), using a Zincke short-stemmed thermometer. He made various salts, the chloride, amide, and anilide of the acid, and finally, by the action of the chloride on benzene and aluminium chloride, he obtained parabenzoyldiphenylsulphone.

In 1900, Canter,(2) working in this laboratory, undertook the study of the analogous compounds in the ortho series. He used commercial orthotoluenesulphone chloride, from which as much of the para chloride as possible had been removed. This he treated with benzene and aluminium chloride and obtained a tolylphenylsulphone which he took to be the ortho compound:



$$C_6H_4\left\langle\begin{matrix}CH_3\\ SO_2Cl\,(o)\end{matrix}\right. + C_6H_6 + (Al_2Cl_2) = C_6H_4\left\langle\begin{matrix}CH_3\\ SO_2C_6H_5\,(o)\end{matrix}\right. + HCl + (Al_2Cl_2).$$

By oxidizing this sulphone with potassium permanganate in water he obtained an acid which should have the same formula as that assigned by Graebe and Schultess to the acid prepared by them by oxidizing phenylthiosalicylic acid with dilute nitric acid:



$$C_6H_4\left\langle\begin{matrix}CH_3\\ SO_2C_6H_5\,(o)\end{matrix}\right. + 3O = C_6H_4\left\langle\begin{matrix}COOH\\ SO_2C_6H_5\,(o)\end{matrix}\right. + H_2O.$$

The acid thus obtained by Canter, which he called orthophenylsulphonebenzoic acid, was distinctly different from the sulphoben-

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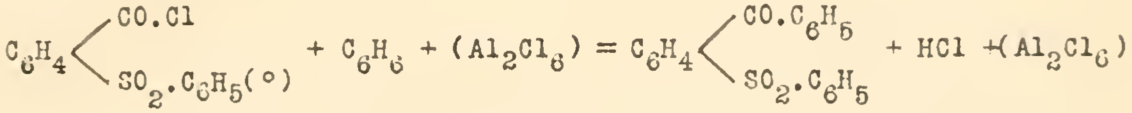
(1) Am. Chem. J. 20, 302.

(2) Am. Chem. J. 25, 96.

zideorthocarbonic acid of Graebe and Schultess. It melted at 267° - 268°, and contained no water of crystallization, while the acid prepared by Graebe and Schultess contained one molecule of water of crystallization and melted at 99°, losing its water of crystallization at 105°, and after dehydrating melted at 152°. Canter also prepared salts of orthophenylsulphonebenzoic acid, besides the chloride, amide, and anilide, and finally, by treatment of the chloride with benzene and aluminium chloride, he obtained orthobenzoyldiphenylsulphone, which he showed to be identical with the substance obtained by Remsen and Saunders,(1) from the mixed chlorides of orthosulphobenzoic acid by treatment with benzene and aluminium chloride:



$$C_6H_4\begin{cases}CO.Cl\\SO_2.C_6H_5(\circ)\end{cases} + C_6H_6 + (Al_2Cl_6) = C_6H_4\begin{cases}CO.C_6H_5\\SO_2.C_6H_5\end{cases} + HCl + (Al_2Cl_6)$$

This last reaction was accepted as proof of the structure of orthophenylsulphonebenzoic acid on the one hand and of orthobenzoyldiphenylsulphone on the other. It remained then to ascertain the cause of the difference between the orthophenylsulphonebenzoic acid of Canter and the sulphobenzideorthocarbonic acid of Graebe and Schultess.

In 1902, Weedon,(2) working in this laboratory, repeated the work of Graebe and Schultess bearing on the formation of sulphobenzideorthocarbonic acid. He prepared phenylthiosalicylic acid by the method of Graebe and Schultess and found its properties to be as described by them. The results of Weedon's investigation of the oxidation of phenylthiosalicylic acid are summarized briefly as follows:

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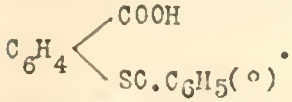
(1) Am. Chem. J. 17, 362.

(2) Dissertation, Johns Hopkins University, 1902.

When phenylthiosalicylic acid is heated with dilute nitric acid several products are formed, the principal one being phenylsulphoxideorthocarbonic acid, which Weedon showed to have the formula,



$C_6H_4\left\langle\begin{matrix}COOH\\ SC.C_6H_5(o)\end{matrix}\right.$.

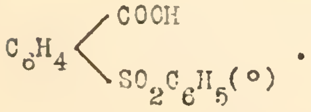
Weedon further states that he obtained the product, melting at 99°, described by Graebe and Schultess, though its separation from phenylsulphoxideorthocarbonic acid is quite difficult. He also found a third product, a pulverulent deposit, difficultly soluble in alcohol, which he did not study.

Weedon was not able to prepare the acid melting at 99° in quantity by the use of dilute nitric acid, but by using concentrated or fuming nitric acid this was almost the sole product. Though it at first appeared to be a definite compound, Weedon found that after several crystallizations two forms of crystals are obtained, one being phenylsulphoxideorthocarbonic acid, and the other an acid melting at 211° - 211.5°, which he did not identify. He found further that these two acids can be obtained from the product melting at 99° by the difference in solubility of their barium salts. He also showed that when the substance which melts at 99° is heated with potassium permanganate in water, a substance is obtained which at first melts at 92° - 94°, but after standing exposed to the air for several days, melts at 180° - 184°. He concludes that this indicates that the acid melting at 99° is a definite compound, which gives a definite oxidation product. As he did not study the substance melting at 180°-184°, this point was left undetermined, but it is evident that the acid described by Graebe and Schultess is not a sulphone, since it can be oxidized and also split up into two constituents, each of which is a well characterized acid.

Weedon then tried the action of potassium permanganate on phenylthiosalicylic acid, expecting that the product would be the orthophenylsulphonebenzoic acid described by Canter. He obtained, however, another acid, which proved to be isomeric with orthophenylsulphonebenzoic acid. Instead of melting at 267° - 268°, it melted at 143°. He made several salts and other derivatives of this acid, and from the chloride he obtained orthobenzoyldiphenylsulphone by the action of benzene and aluminium chloride. This he showed to be identical with the product obtained by Remsen and Saunders(1) and also by Canter.(2)

Weedon also found that the acid thus prepared by oxidizing phenylthiosalicylic acid with potassium permanganate loses one molecule of water when heated with concentrated sulphuric acid, and condenses to benzophenonesulphone.

From the analyses of the acid, and from its reactions, Weedon considered it to be isomeric with the acid described by Canter, and he named it phenylsulphoneorthocarbonic acid, its formula being:



$$C_6H_4\left\langle\begin{matrix}COOH\\SO_2C_6H_5(o)\end{matrix}\right. .$$

Thus there appeared to be two isomeric acids of this formula. No simple theory could be framed which would account in a satisfactory manner for the existence of two such compounds, and, at the suggestion of President Remsen, the work herein described was undertaken in order, if possible, to find an explanation of this apparent isomerism.

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(1) loc. cit.

(2) loc. cit.

II. PRODUCTS OBTAINED BY OXIDIZING PHENYLTHIOSALICYLIC ACID WITH NITRIC ACID.

Plainly the first point to be settled was the formation and structure of the acid described by Weedon and named by him phenylsulphoneorthocarbonic acid. It was also necessary to establish his claim that the sulphobenzideorthocarbonic acid, described by Graebe and Schultess is not a sulphone and therefore has not the formula which they assigned to it. The reactions used in preparing these compounds were the same as those employed by Graebe and Schultess and later by Weedon.

Thiophenol was prepared by the method used by Weedon,(1) from benzenesulphone chloride. The thiophenol used was colorless and boiled at 168° (uncorr.).(2)

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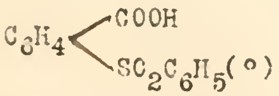
(1) loc. cit.

(2) The experience of the writer with thiophenol leads him to give a brief description of its physiological effects. As is well known, in concentrated form it produces severe burns, but even after a momentary contact with the skin, very unpleasant and even dangerous effects may follow. After ten days or even more, an eruption appears at the point of contact, accompanied by severe itching. The affected part becomes red and much swollen, suppurating pustules appear, and in severe cases, symptons of blood poisoning manifest themselves. The treatment is, in general, that for a severe burn: exclusion of air and moisture and use of an antiseptic ointment. The vapors of thiophenol, when present in considerable amount, produce giddiness and headache, and have a remarkable effect upon the eyes. The lids droop, and it is impossible to open them. After a few minutes in the fresh air, this effect passes off, but the eyes remain very sensitive to light.

Phenylthiosalicylic acid was prepared by the method of Graebe and Schultess,(1) from anthranilic acid and thiophenol. Weedon(2) also prepared it in the same manner. It was found that the use of glacial acetic acid as a solvent effects the purification of the acid rather more easily than alcohol, and it was therefore used in purifying the acid prepared for this work. The acid thus prepared was almost colorless and melted at 166° (uncorr.) = 170° (corrected).(3) A small sample was sublimed and as thus obtained was pure white, but the melting point was not changed.

1. Oxidation of Phenylthiosalicylic Acid by Means of Dilute Nitric Acid.

Graebe and Schultess(1) state that when phenylthiosalicylic acid was heated with dilute nitric acid, (one part concentrated nitric acid to two parts water) they obtained an acid which crystallized from alcohol in white needles, containing one molecule of water of crystallization and melting at 99°. At 105° this substance lost its water of crystallization and after being dehydrated it melted at 152°. From the method of its formation and the results of analyses they called it sulphobenzideorthocarbonic acid and considered its formula to be:



$C_6H_4\left<\begin{matrix}COOH\\ SO_2C_6H_5(o)\end{matrix}\right.$

. They did not make any salts or other derivatives of the acid.

Weedon(2) repeated the work of Graebe and Schultess on this subject and obtained as a product of treating phenylthiosalicylic

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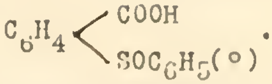
(1) loc. cit.
(2) loc.cit.
(3) The thermometer used in this work was carefully calibrated before using by the method of Crafts.

acid with dilute nitric acid, an acid which he identified as phenylsulphoxideorthooarbonic acid, having the formula:  $C_6H_4<\begin{matrix}COOH\\SOC_6H_5(o)\end{matrix}$.

He found that when this acid is crystallized from somewhat dilute alcohol it crystallizes in two forms, one of which has one molecule of water of crystallization and crystallizes in very slender, silky, white needles which melt at 80°-85°, lose water of crystallization at 105°, and, after dehydration, melt at 163°. The other form is anhydrous, crystallizes in rhombic prisms and melts at 163°. Besides this acid Weedon also obtained a very small amount of the product described by Graebe and Schultess, and also a very small quantity of another acid which he did not study at all, as it was formed in such minute quantity. He made various salts of phenylsulphoxideorthocarbonic acid, and also oxidized it by means of potassium permanganate, obtaining phenylsulphoneorthocarbonic acid as the result of this reaction.

The oxidation of phenylthiosalicylic acid by means of dilute nitric acid was also studied to some extent during the present investigation, the results agreeing in general with those of Weedon, so far as the work was carried.

The acid described by Graebe and Schultess was found to be formed in very small quantity, if at all, by the use of dilute nitric acid. A product was obtained melting at 99°, but on treating it with cold absolute methyl alcohol most of it dissolved, leaving a residue which melted at 163° and was anhydrous phenylsulphoxideorthocarbonic acid. The corrected melting point of the anhydrous form of this acid is 167°. As Weedon states, the hydrous and anhydrous forms of this acid occur together, crystallizing from the same solution, and mixtures of them give melting points ranging from 85° to 100°, so that

it is very difficult to say that the acid described by Graebe and Schultess is formed. It was not possible to isolate it.

2. Oxidation of Phenylthiosalicylic Acid by means of Fuming Nitric Acid.

Weedon found that when phenylthiosalicylic acid is treated with fuming nitric acid without heating, the acid described by Graebe and Schultess, melting at 99°, is formed and is almost the entire product of the reaction. He found, further, that while it at first appears to be an individual compound, when recrystallized from alcohol four or five times it is separated into two substances. One of these is deposited in the form of white needles, and the other as a white, pulverulent substance, which is less soluble in tepid alcohol than the white needles and can thus be separated from them. He showed that the substance crystallizing in needles is phenylsulphoxideorthocarbonic acid. The pulverulent substance when recrystallized from alcohol gave leaflets melting at 211°-211.5°. The substance is an acid. Weedon did not identify it.

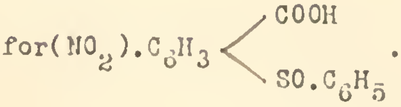
On repeating Weedon's work it was found that the acid melting at 211°-211.5° is formed only to a small extent under the conditions with which he worked, but by boiling the solution of phenylthiosalicylic acid in fuming nitric acid for some time, the yield was much increased. As a result of several experiments the following method was adopted.

Ten grams of phenylthiosalicylic acid are placed in a small flask, and 20 cc. of fuming nitric acid are added gradually. After the first violent action has subsided, and the phenylthiosalicylic acid has dissolved, the flask is attached to a reflux con-

denser and heated on the water bath for three hours. After cooling, the solution is poured into cold water. A yellow oil separates, which partially solidifies after several hours. The sticky, semi-solid mass is heated in an air bath at 110° for an hour and is then dissolved in boiling benzene, in which it is difficultly soluble. From this solution small, colorless crystals separate, together with a gummy product which adheres to them. The mother liquor is poured off, and the crystals are washed with small portions of boiling benzene, which removes the gummy substance. The crystals as thus obtained melt at 216° (uncorr.), the corrected melting point being 222°. Weedon found 211°-211.5° (uncorr.) as the melting point, but it is probable that the acid as prepared by him contained some phenylsulphoxideorthocarbonic acid, which it is very difficult to remove by crystallizing from alcohol.

Weedon made the barium salt of the acid melting at 211° - 211.5° and found it to contain 18.80 per cent of barium. He suggested that this is not far from the figure required by the formula of the phenyl ester of orthosulphobenzoic acid, but considered this only as a possibility. If the action of fuming nitric acid should be to introduce a nitro group into phenylthiosalicylic acid, as well as to oxidize it to the sulphoxide condition, the barium salt of the mononitrophenylsulphoxideorthocarbonic acid thus formed should contain 19.22 per cent. of barium, which corresponds quite well with the result obtained by Weedon. A qualitative test of the acid melting at 216° indicated the presence of nitrogen, and a determination of nitrogen by the absolute method of Dumas gave the following results:

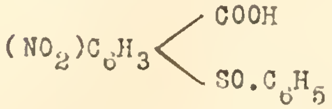
0.2437 gram gave 10.05 cc. = 0.01258 gram of nitrogen.



$(NO_2).C_6H_3<\begin{matrix}COOH\\SO.C_6H_5\end{matrix}$

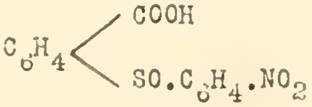
Percentage.	Calculated for $(NO_2).C_6H_3<\begin{matrix}COOH\\SO.C_6H_5\end{matrix}$.	Found.
N	4.82	5.15

From this it is evident that the acid melting at 216° (uncorr.) is a mono nitro derivative of phenylsulphoxideorthocarbonic acid. No attempt was made to determine the position of the nitro group. The formula of the acid may be



$(NO_2)C_6H_3<\begin{matrix}COOH\\SO.C_6H_5\end{matrix}$

or



$C_6H_4<\begin{matrix}COOH\\SO.C_6H_4.NO_2\end{matrix}$.

When the benzene mother liquor, from which the nitro compound had crystallized, was evaporated to dryness, a gummy substance remained. This was dissolved in boiling ethyl acetate, from which a relatively large quantity of small white leaflets crystallized on cooling. This substance melted at 163° (uncorr.) and was phenylsulphoxideorthocarbonic acid.

It was found that a mixture of phenylsulphoxideorthocarbonic acid with a small proportion of the mono nitro derivative of this acid crystallizes from alcohol in white needles, melting at 99°, losing water at 105°, and melting again at 152°. It appears from this that the acid described by Graebe and Schultess, melting at 99°, is not a definite compound, but a mixture of phenylsulphoneorthocarbonic acid and a mononitrophenylsulphoxideorthocarbonic acid.

The yield of nitrophenylsulphoxideorthocarbonic acid is small even when the method of preparation just described is used, and an attempt was, therefore, made to increase the proportion in which it is formed.

Phenylthiosalicylic acid was treated with fuming nitric acid as before. The solution was cooled and two volumes of concentrated sulphuric acid were added. The flask was then attached to a reflux condenser and heated for three hours on the water bath. After cooling the reaction mixture was poured into cold water. A yellowish white, semi-solid mass separated. The acid solution was poured off and the gummy mass was boiled with a little water, to remove the nitric and sulphuric acids. After cooling the gummy mass was removed and dried in an air bath at 130° for several hours. It then solidified on cooling. It was pulverized and boiled with benzene. Most of the material dissolved, and the residue was filtered off, and dissolved in alcohol, from which it separated, on addition of water, in very small white crystals melting at about 208°. The product was evidently not pure, and it was not found possible to purify it. The barium salt was made, and analysis indicated that the acid was a mixture of dinitro- and trinitrophenylsulphoxideorthocarbonic acids, with, perhaps, some of the mono nitro compound. The results of the analyses were as follows:

0.2436 gram air-dried salt lost 0.0271 gram H_2O at 180°.

H_2O - - - - - - - - - - - - - - - - 11.12.

I. 0.1793 gram anhydrous salt gave 0.0489 gram $BaSO_4$.

II. 0.1271 gram anhydrous salt gave 0.0349 gram $BaSO_4$.

Percentage	Calculated for		Found.	
	$(C_{13}H_8O_3S(NO_2)_2)_2Ba$	$(C_{13}H_7O_3S(NO_2)_3)_2Ba$	I.	II.
Ba	17.02	15.28	16.05	16.06.

The acid product melting at about 208° was analysed for nitrogen by the absolute method.

0.1845 gram gave 15.00 cc. nitrogen = 0.0173 gram nitrogen.

Percentage	Calculated for		Found
	$C_{13}H_8O_3S(NO_2)_2$	$C_{13}H_8O_3S(NO_2)_3$	
N	8.36	12.53	9.39

Owing to lack of time this product was not studied further.

III. PHENYLSULPHONEORTHOCARBONIC ACID.

As stated above, this acid was first made by Weedon(1) in 1902 by oxidizing phenylthiosalicylic acid with potassium permanganate in water. In order to establish its formula he made analyses of the acid and of several of its salts. He also made the chloride and amide, and from the chloride he obtained orthobenzoyldiphenyl sulphone by the action of benzene and aluminium chloride. He also heated phenylsulphoneorthocarbonic acid with concentrated sulphuric acid and obtained benzophenonesulphone.

The phenylsulphoneorthocarbonic acid used in this investigation was made by the method described by Weedon. By heating phenylthiosalicylic acid with a slight excess of potassium permanganate in a large excess of water, filtering from the oxides of manganese, and acidifying the filtrate, as directed by Weedon, a product was obtained which had the properties which he describes. On acidifying the filtrate, this acid is precipitated as a pale yellow oil, which solidifies on standing. This product is easily soluble in methyl, ethyl, and propylalcohols, ether, glacial acetic acid and acetone, but does not crystallize well from these solvents, being deposited usually as a syrup. It is also difficultly soluble in boiling water. The best solvent from which to crystallize it is benzene, in which it is easily soluble, but to a much less extent than in alcohol. From benzene it crystallizes in short, thick, colorless needles, radially grouped, which are anhydrous, and melt at 143° (uncorr.). Corrected

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(1) loc. cit.

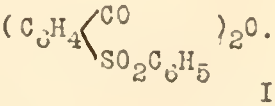
for exposed stem of thermometer, the melting point is 140°. From water the acid crystallizes in clear prisms which melt at 51.5° and contain 1 1/2 molecules of water of crystallization.

The chloride of this acid was prepared in the usual way, by the action of phosphorus pentachloride on the acid. The reaction takes place smoothly at about 45°. The chloride is easily soluble in ether and crystallizes from this solvent in long, clear, colorless prisms or needles, which, as first obtained, melt at 75°-76° (uncorr.). After repeated crystallization from ether the melting point is 79° (uncorr.); 80° (corr.). It is very difficult to remove the last traces of phosphorus oxychloride, and this doubtless explains the lower melting point given by Weedon, who found it to be 75°-76° (uncorr.). The chloride is very stable. It is not acted on by cold dilute alkali. It is difficultly soluble in boiling dilute alkali, and from this solution phenylsulphoneorthocarbonic acid is precipitated on acidifying. A sample of the chloride was exposed to the air for three weeks, but the melting point was not changed.

Anhydride of Phenylsulphoneorthocarbonic Acid. Weedon mentions another product of the reaction of phosphorus pentachloride with phenylsulphoneorthocarbonic acid. He describes this very briefly as being a chloride which is formed by heating the mixture of phosphorus pentachloride and phenylsulphoneorthocarbonic acid to 200°. He gives the melting point of this product as 121°-123°, but owing to the lack of time he did not study it further. Efforts were made to obtain this second chloride during the course of this investigation, but without success, and it appears probable that what Weedon really obtained was a mixture of the anhydride, now to be described, and the chloride. It was found, as a result of numerous experiments,

that when a considerable excess of phosphorus pentachloride is used, the result is not in the least affected by heating to 200°, even for several hours. The chloride melting at 79° is the only product formed. If, however, an excess of phenylsulphoneorthocarbonic acid is used, the result is quite different. Besides the chloride a product is formed which is practically insoluble in ether, and which is thus easily separated from the chloride. The new product is soluble in acetone, benzene, and alcohol. From acetone it crystallizes in elongated rhombic crystals, and in small square plates and prisms, melting at 143°. From benzene it crystallizes in very small, clear crystals, to which no definite form could be ascribed, melting at 143° (uncorr.). The substance is not soluble in alkali even on boiling. It does not contain chlorine. Analysis gave results as follows:

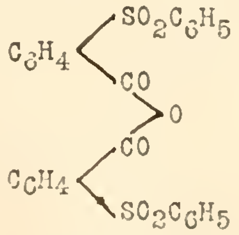
I. 0.2483 gram gave 0.5580 gram CO_2 and 0.0678 gram H_2O.
II. 0.2408 gram gave 0.5483 gram CO_2 and 0.0760 gram H_2O.
III. 0.3035 gram gave 0.6901 gram CO_2 and 0.0909 gram H_2O.

Percentage.	Calculated for  $\left(C_6H_4\left<\begin{matrix}CO\\SO_2C_6H_5\end{matrix}\right.\right)_2O$.	Found.		
		I.	II.	III.
C	61.64	61.28	62.09	62.00
H	3.58	3.03	3.50	3.35

The only compound capable of formation under these conditions having a formula in accordance with the results of these analyses is the anhydride of phenylsulphoneorthocarbonic acid. The formation of this compound under the conditions mentioned is easily explained. Doubtless the first action is between phenylsulphoneorthocarbonic acid

and phosphorus pentachloride to form the chloride of phenylsulphoneorthocarbonic acid. This in turn reacts with the excess of phenylsulphoneorthocarbonic acid to form the anhydride, a molecule of hydrochloric acid being liberated in the reaction.

To test the correctness of this explanation, a mixture of 1 gram of the chloride of phenylsulphoneorthocarbonic acid with 1.3 grams of phenylsulphoneorthocarbonic acid was placed in a dry test tube in a sulphuric acid bath, and heated to 135°-150° for several hours. The mass became liquid and hydrochloric acid was evolved freely. After about three hours the tube was removed from the bath and allowed to cool. The contents solidified to a dark brown crystalline mass, which was dissolved in boiling benzene, boiled with animal charcoal, and filtered. On cooling, small, irregularly shaped, colorless crystals separated, which melted at 143°, and were identical with those obtained as described above. From this experiment and the results of the analyses there can be no doubt that the compound is really the anhydride of phenylsulphoneorthocarbonic acid, and that its formula is:

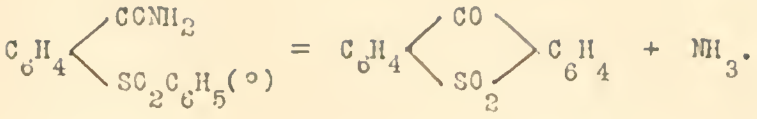


$$C_6H_4\langle{}^{SO_2C_6H_5}_{CO}\rangle O \langle{}^{CO}_{SO_2C_6H_5} C_6H_4$$

This anhydride is exceedingly stable towards alkali. Boiled for an hour with strong caustic soda, there was no perceptible change in it. It dissolved in concentrated sulphuric acid, and when this solution is heated to 130° for ten hours the anhydride is converted into benzophenonesulphone. The product thus obtained was identical with that obtained by similar treatment of phenylsulphone-

orthocarbonic acid, and also with that obtained by oxidizing thioxanthone. The anhydride is soluble in boiling alcohol from which it crystallizes in small, hard, colorless crystals, which melt at 145°, while the crystals from the benzene solution melt at 143°. When equal portions of the anhydride crystallized from benzene and from alcohol are mixed, the melting point of the mixture is 144°. The corrected melting point of the anhydride crystallized from benzene is 146°. Crystallized from alcohol, 148°.

Amide of Phenylsulphoneorthocarbonic Acid. When the chloride of this acid is allowed to stand with concentrated ammonia at ordinary temperature for 24 hours, the amide is formed, an appreciable amount of heat being evolved during the first few minutes. The solid product thus obtained is filtered from the ammoniacal solution, washed, and dissolved in boiling water, filtering, if necessary, from any unchanged chloride which may be present. On cooling, the amide crystallizes in slender, pure white needles, which form a semi-solid mass in the beaker if the solution is not too dilute. These crystals melt at 171°-171.5°(uncorr.). The corrected melting point is 175°-175.5°. As is the case with all the derivatives of phenylsulphoneorthocarbonic acid, the amide is a very stable compound. It was found to be impossible to make a satisfactory determination of nitrogen by the Kjeldahl method, or by the Gunning modification, using sulphuric acid and potassium sulphate. When the latter method was used benzophenonesulphone sublimed into the upper portion of the digestion flask and was deposited in very fine crystals. This reaction may be expressed in this manner:



$$C_6H_4\left\langle\begin{array}{l}CONH_2\\SO_2C_6H_5(o)\end{array}\right. = C_6H_4\left\langle\begin{array}{l}CO\\SO_2\end{array}\right\rangle C_6H_4 + NH_3.$$

Determinations of nitrogen by the Gunning modification of the Kjeldahl method gave results which were too low, by about 0.5 per cent., but the result was not uniform, some determinations giving results as much as one per cent. too low.

A determination of nitrogen by the absolute method of Dumas gave a better result.

0.4315 gram of amide gave 17.4 cc. of nitrogen (under standard conditions) = 0.02176 gram of nitrogen.

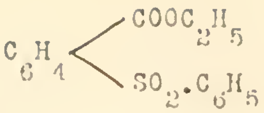
Percentage.	Calculated for $C_6H_4\left\langle\begin{array}{l}CONH_2\\SO_2C_6H_5\end{array}\right.$.	Found.
N	5.37	5.16

Ethyl Ester of Phenylsulphoneorthocarbonic Acid. Two grams of the chloride of this acid were boiled for a few minutes with about 50 cc. of absolute ethylalcohol. The chloride was easily dissolved. Water was added until precipitation was almost effected, and the solution was allowed to cool. Bunches of colorless, feathery needles, radially grouped, separated out after standing a short time. These crystals melted at 77°-78°(uncorr.). Corrected melting point, 78°-79°.

The ethyl ester is saponified with some difficulty by boiling with a ten per cent. solution of caustic soda.

Analysis by combustion gave results as follows:

0.2317 gram of ester gave 0.5234 gram CO_2 and 0.1029 gram H_2O.

Percentage.	Calculated for  $C_6H_4\begin{matrix}\diagup COOC_2H_5\\ \diagdown SO_2.C_6H_5\end{matrix}$	Found.
C	62.06	61.58
H	4.83	4.93

Methyl Ester of Phenylsulphoneorthocarbonic Acid. The chloride was boiled with ethyl alcohol and water was added to the solution, which was then allowed to cool. A slightly yellowish oil separated, which solidified on standing. Long prismatic crystals also appeared, which were grouped so as to resemble plates. Recrystallization from methyl alcohol gave rectangular plates arranged in tiers, so as to resemble a roof, the top plate being much smaller than the bottom plate, and the series forming steps. These crystals melted at 63°. No analysis of this compound was made.

As has been stated, Graebe and Schultess(1) prepared thioxanthone from phenylthiosalicylic acid by heating this acid with concentrated sulphuric acid. They oxidized thioxanthone with chromic acid and obtained benzophenonesulphone. Weedon(2) found that when phenylsulphoneorthocarbonic acid is heated for 14 hours with concentrated sulphuric acid, a similar condensation is affected and benzophenonesulphone is formed. These experiments were repeated in the course of the present investigation and the statements of Graebe and Schultess and of Weedon were confirmed. Both methods led to the formation of a substance which crystallized from alcohol in long, slender, pale greenish yellow prisms, melting at 185° (uncorr.) or 189.5° (corrected).

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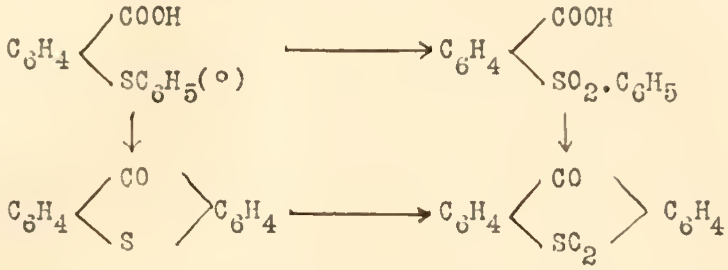
(1) loc. cit.

(2) loc. cit.

A mixture of the two specimens of benzophenonesulphone prepared by these two methods showed no change in the melting point, showing them to be identical. When boiled with an alcoholic solution of caustic potash both specimens gave the characteristic color test for benzophenonesulphone. On boiling the solution becomes a beautiful blue in color, resembling the starch-iodine blue, which fades away on cooling, leaving the solution clear and colorless. These transformations may be represented thus:



A further proof of the relation between phenylthiosalicylic acid and phenylsulphoneorthocarbonic acid is furnished by the following experiment.

a.- An intimate mixture of phenylthiosalicylic acid with six times its weight of powdered lime was heated in a small retort. A yellow oil distilled over, and feathery needles also appeared in the distillate, these being due, probably, to the sublimation of some phenylthiosalicylic acid. The distillate was washed with a solution of sodium carbonate to remove this unchanged phenylthiosalicylic acid. The yellow oil was extracted with ether, dried, and distilled. After the ether had distilled off thethermometer rose rapidly to 286°. The portion which came over between 286° and 292° was collected. Pure phenylsulphide boils at 292.5°, according to Stenhouse. The distillate was a yellow oil and had an odor suggestive of volatile sulphides. It was dissolved in strong sulphuric acid and warmed

gently. Chromic anhydride was added in small portions until the solution showed a reddish color. The reaction mixture was then poured into cold water; the yellow precipitate which was formed was filtered off, washed, dried, and dissolved in benzene, from which it crystallized in rhombic plates. Recrystallized from alcohol the product was obtained pure, in the form of colorless, rhombic plates which melted at 124° (uncorr.); 126° (corrected).

b.- In the same manner, phenylsulphoneorthocarbonic acid was heated with lime. A yellow oil distilled over, which solidified, on cooling, to a yellow crystalline mass. This was dissolved in benzene, from which solution it crystallized in rhombic plates. These were dissolved in alcohol, from which the pure product crystallized in colorless, rhombic plates, melting at 124° (uncorr.); 126° (corrected).

A mixture of the two specimans thus prepared, melting at 124°, showed no change in melting point.

The melting point of pure diphenylsulphone is 123.75° (uncorr.).(1)

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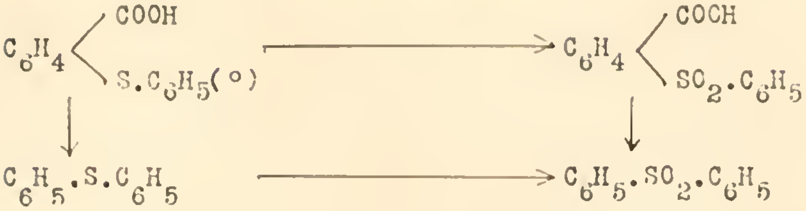
(1) The question of the melting point of diphenylsulphone has been very carefully investigated by Mr. Bradshaw, working in this laboratory during the present year. He found that the melting point is 123.75° (uncorr.) no matter by what method the sulphone is obtained, if the purification is complete. The melting point of diphenylsulphone is variously recorded, the values ranging from 124° to 128° (uncorr.).

The results of this experiment may be expressed thus:



$$\begin{tikzcd}
C_6H_4\left\langle\begin{matrix} COOH \\ S.C_6H_5(o) \end{matrix}\right. \arrow[r] \arrow[d] & C_6H_4\left\langle\begin{matrix} COCH \\ SO_2.C_6H_5 \end{matrix}\right. \arrow[d] \\
C_6H_5.S.C_6H_5 \arrow[r] & C_6H_5.SO_2.C_6H_5
\end{tikzcd}$$

Considering the results in connection with the formation of benzophenonesulphone as described above, there can be no doubt that the structure of phenylsulphoneorthocarbonio acid is really as represented by Weedon.

Molecular Weight of Phenylsulphoneorthocarbonic Acid. Determinations of the molecular weight of phenylsulphoneorthocarbonic acid in benzene and in alcohol gave results as follows:

I. 1.2800 grams of phenylsulphoneorthocarbonic acid dissolved in 38.8300 grams of absolute ethyl alcohol raised the boiling point 0.142° (corrected for height of barometer), corresponding to a molecular weight of 266.

II. 0.3600 gram of phenylsulphoneorthocarbonic acid dissolved in 42.8700 grams of anhydrous, thiophene free benzene raised the boiling point 0.082°, corresponding to a molecular weight of 283.

III. 0.8981 grams of phenylsulphoneorthocarbonic acid dissolved in 42.8700 grams of anhydrous, thiophene free benzene raised the boiling point 0.211°, corresponding to a molecular weight of 275.

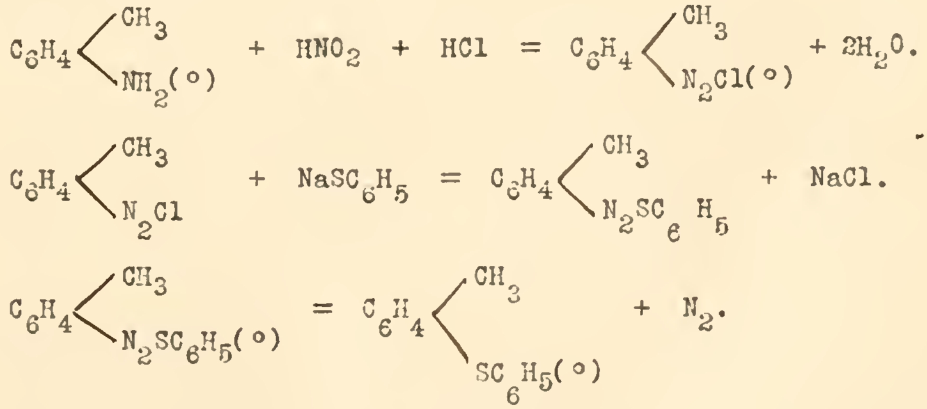
The calculated molecular weight of phenylsulphoneorthocarbonic acid is 260.18, the atomic weight of hydrogen being unity.

IV. OXIDATION OF ORTHOTOLYLPHENYL SULPHIDE.

As the acid obtained by Canter had resulted from the oxidation of the methyl group of orthotolylphenylsulphone, and the acid obtained by Weedon, i.e. phenylsulphoneorthocarbonic acid, had been formed by the oxidation of the sulphide grouping of phenylthiosalicylic acid, it was thought possible that by simultaneous oxidation of both groups it might be possible to obtain both products. For this purpose orthotolylphenyl sulphide was prepared by the method of Graebe and Schultess.(1)

1. Orthotolylphenyl Sulphide.

The method employed in the preparation of this compound is entirely analogous to that used in preparing phenylthiosalicylic acid. The reactions are,



$$1.\quad C_6H_4\left<\begin{matrix}CH_3\\ NH_2(\circ)\end{matrix}\right. + HNO_2 + HCl = C_6H_4\left<\begin{matrix}CH_3\\ N_2Cl(\circ)\end{matrix}\right. + 2H_2O.$$

$$2.\quad C_6H_4\left<\begin{matrix}CH_3\\ N_2Cl\end{matrix}\right. + NaSC_6H_5 = C_6H_4\left<\begin{matrix}CH_3\\ N_2SC_6H_5\end{matrix}\right. + NaCl.$$

$$3.\quad C_6H_4\left<\begin{matrix}CH_3\\ N_2SC_6H_5(\circ)\end{matrix}\right. = C_6H_4\left<\begin{matrix}CH_3\\ SC_6H_5(\circ)\end{matrix}\right. + N_2.$$

The orthotoluidine used was redistilled twice before using. It boiled at 195°-196°.

31 grams of orthotoluidine were mixed with 64 cc. of concentrated hydrochloric acid and 100 cc. of water, in a thick walled beaker which was surrounded by crushed ice. To this mixture was

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(1) loc. cit.

added, in small portions, 22 grams of sodium nitrite dissolved in 100 cc. of water, the temperature being kept below 5° by dropping crushed ice into the beaker. The diazo solution thus prepared was run in a thin stream from a dropping funnel into a solution of 34 grams of thiophenol and 60 grams of caustic soda in 300 cc. of water, the temperature of this solution being 50°-60°, in order to decompose the diazothiophenol ether as soon as formed. A finely divided yellow precipitate was formed and gas was evolved. The precipitate disappeared on stirring. After all the diazo solution had been added, the mixture was heated slowly on the water bath until no more gas was evolved. Care must be taken not to heat too rapidly, as the evolution of gas may be so violent as to be almost explosive. As the heating progressed a red oil separated and sank to the bottom. After cooling, this was drawn off by means of a separating funnel and dissolved in ether. The solution was dried over fused potassium carbonate and then distilled. After distilling off the ether the thermometer rose rapidly to 290° and the portion boiling at 290°-302° was collected. This was redistilled and the portion boiling at 300°-305° was collected. According to Graebe and Schultess pure orthotolylphenyl sulphide boils at 304.5°. The thermometer used in this distillation was a nitrogen filled mercury thermometer, graduated to 550°, so that there was no correction for exposed stem.

Orthotolylphenyl sulphide as thus obtained is a pale yellow, mobile, highly refractive liquid, having a disagreeable odor suggestive of hydrogen sulphide. On long standing it becomes dark reddish brown in color.

2. Oxidation of Orthotolylphenyl Sulphide.

Fifteen grams of orthotolylphenyl sulphide were suspended in 2 1/2 liters of boiling water contained in a 5 liter round flask, which was heated in boiling water. Steam was passed into the flask continuously. During the first hour of heating 25 grams of very finely powdered potassium permanganate were added in small portions. The heating was continued for 16 hours. A few cubic centimeters of alcohol were added to reduce the excess of potassium permanganate, the precipitated oxides of manganese were filtered off, and the filtrate was evaporated to a volume of 500 cc. It was then acidified with strong hydrochloric acid. A pale yellowish oil and white crystals were precipitated, the oil becoming solid after standing for some hours. This product was dissolved in hot benzene, from which it crystallized on cooling in bunches of short, colorless needles, radially grouped, which melted at 143° (uncorr.) When a portion of these crystals was mixed with an equal portion of phenylsulphoneorthocarbonic acid, prepared as above from phenylthiosalicylic acid, the melting point of the mixture was the same, viz., 143° (uncorr.); 146° (corrected).

Analysis of the substance for carbon and hydrogen by combustion gave results as follows:

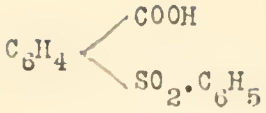
I. 0.3762 gram gave 0.8173 gram CO_2 and 0.1316 gram H_2O.

II. 0.2984 gram gave 0.6519 gram CO_2 and 0. 1065 gram H_2O.

Analysis of the substance for sulphur by the method of Liebig gave results as follows:

III. 0.3935 gram gave 0.3525 gram $BaSO_4$.

IV. 0.3878 gram gave 0.3429 gram $BaSO_4$.

Percentage	Calculated for  $C_6H_4<^{COOH}_{SO_2.C_6H_5}$	Found.			
		I.	II.	III.	IV.
C	59.51	59.25	59.57		
H	3.85	3.82	3.96		
S	12.23			12.05	12.12

From these results it is evident that phenylsulphoneorthocarbonic acid is also formed by the oxidation of orthotolylphenyl sulphide by means of potassium permanganate. No trace of the acid described by Canter could be found in the products of reaction.

V. THE ACID DESCRIBED BY CANTER, AND CALLED BY HIM, ORTHOPHENYLSULPHONEBENZOIC ACID.

As has been stated, this acid was described by Canter(1) in 1901. He obtained it by oxidizing orthotolylphenylsulphone by means of potassium permanganate, and from its method of preparation, as well as from the results of analyses made by him, it should have the same formula as the compound to which Weedon gave the name phenylsulphoneorthocarbonic acid. A careful study of the latter compound having confirmed the correctness of this formula for phenylsulphoneorthocarbonic acid, it remained to repeat the work of Canter, in the hope that some additional light might thus be had on the problem.

The orthotolylphenylsulphone used in this work was prepared by the method of Canter.(1) The orthotoluenesulphone chloride which was used in its preparation was that which remained from Canter's work and was originally supplied by the chemical factory of von Heyden.

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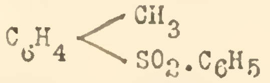
(1) loc. cit.

By treating this material with benzene and aluminium chloride in the manner described by Canter, a product was obtained which crystallized from alcohol in white leaflets, melting at 67.5°-68° (uncorr.), as stated by him. He analysed the substance and obtained results in accord with the formula  $C_6H_4 \begin{cases} CH_3 \\ SO_2.C_6H_5 \end{cases}$. It is soluble in petroleum ether, ordinary ether, benzene, alcohol, glacial acetic acid, and in strong nitric acid, from which it is recovered unchanged by adding water. This substance will be considered again in another connection.

1. Preparation of So-called Orthophenylsulphonebenzoic Acid.

The method described by Canter was followed closely in preparing this substance. The following directions are quoted from his description.(1)

" Ten grams of orthotolylphenylsulphone were suspended and partially dissolved in 2 1/2 liters of boiling water. Into the flask steam was continuously conducted to prevent bumping and to keep the water hot. Finely powdered potassium permanganate in quantity slightly in excess of the calculated amount was added in small spoonfuls throughout the space of an hour and a half. The boiling was continued for 15 hours, till the contents of the flask became quite black and a small portion removed and filtered appeared quite clear. A few cubic centimeters of alcohol were added, the liquid was filtered from the manganese dioxide and evaporated to the volume of one liter. Upon addition of hydrochloric acid the acid was precipitated as a white, flocculent mass. If precipitated from a cold solution, it

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(1) loc. cit.

"shows more of a crystalline structure. The acid was recrystallized from alcohol, but it was hardly possible to obtain it pure in this way, because of the presence of some unchanged sulphone. The barium salt of the acid was made, but even this carried with it some sulphone. The solution of the barium salt was then evaporated to dryness, and the dry salt was treated several times with boiling alcohol. In this manner the remaining small portions of the sulphone were removed. The remaining barium salt was recrystallized and from this the free acid was obtained. This was purified by recrystallization from ordinary alcohol.

" Orthophenylsulphonebenzoic acid crystallizes in clear, small plates, frequently grouped in clusters. It is insoluble in water, and readily soluble in alcohol. A portion heated for an hour and a half in an air bath at a temperature of 130° lost nothing in weight. The acid as above obtained melts at 267°-268° (uncorr.)."

By following these directions as closely as possible an acid was obtained which melted at 267°, but the yield of pure product was astonishingly small. This was the more surprising, as the amount of barium salt obtained, before treating with boiling alcohol, was very considerable, and was in a fair proportion to the amount of sulphone used, but after further purification by the method of Canter less than half a gram of the pure acid melting at 267° was obtained from 10 grams of the sulphone. It was also noticed that the barium salt is completely soluble in boiling alcohol, if enough of this solvent is used.

Other methods of oxidation were tried, in the hope of increasing the yield. Ammonium persulphate, potassium persulphate,

sodium peroxide, and chromyl chloride were tried in turn, but none of these reagents effected a satisfactory oxidation. Persulphates destroyed the sulphone entirely. Sodium peroxide had no effect on it, nor had chromyl chloride in carbon bisulphide solution. After these attempts, the preparation of the acid was continued by the method of Canter.

By heating the acid melting at 267° with lime, diphenyl sulphone was obtained, as in the case of phenylsulphoneorthocarbonic acid.

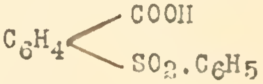
An attempt was also made to condense the acid melting at 267° to benzophenonesulphone by heating with concentrated sulphuric acid. The acid dissolved in concentrated sulphuric acid, forming a brown solution, but no fluorescence was noticeable. After heating this solution for 14 hours at 140° it was cooled and poured into water. A white precipitate formed, which dissolved almost entirely in alkaline carbonate or ammonia. When the filter through which this solution had been passed was boiled with alcoholic potash the blue color characteristic of benzophenonesulphone appeared, fading entirely when the solution was cooled. The amount of benzophenonesulphone formed was so small that a less sensitive test than this would hardly have shown its presence. There was not enough to be removed from the filter. The filter itself had to be boiled with alcoholic potash.

An effort was now made to recover the "unchanged sulphone", which, according to Canter's description, should be found in the alcoholic mother liquors from the first crystallization of the acid and also in the alcoholic washings from the barium salt. From the

alcoholic mother liquors an acid was obtained which did not crystallize from alcohol, but, when the solution was greatly diluted with water or concentrated by evaporation, this product separated as a syrup. It was evaporated to dryness and dissolved in benzene, from which solvent it crystallized in bunches of short, clear needles, radially grouped and melting at 143° (uncorr.). A mixture of a portion of these crystals with an equal portion of phenylsulphoneorthocarbonic acid had the same melting point. The washings from the barium salt referred to above contained the barium salt of the acid melting at 143°. No orthotolylphenylsulphone was found in either solution. From this it appears that phenylsulphoneorthocarbonic acid is formed at the same time as the acid described by Canter, and a comparison of the quantity of each showed that fully 90 per cent. of the yield is phenylsulphoneorthocarbonic acid, which is the substance which Canter supposed to be "unchanged sulphone". The small yield which is obtained of the acid described by Canter is thus fully explained. It is also clear why a trace of benzophenonesulphone was found after heating this acid with concentrated sulphuric acid. This suggested a method of purifying the acid described by Canter. Since benzophenonesulphone is insoluble in alkalies, it is easily removed from the acid by treating the reaction product with alkali, filtering the solution of the alkali salt from the insoluble benzophenonesulphone and reprecipitating the acid by means of hydrochloric acid. An easier and much more satisfactory means of separating the two acids, however, is boiling water. By repeated boiling of the mixture with fresh portions of water, all of the phenylsulphoneorthocarbonic acid is dis-

solved, while the other acid is not. The acid melting at 267° is almost entirely insoluble in boiling benzene, thus giving another means of separation, since phenylsulphoneorthocarbonic acid is easily soluble in this solvent.

It now remained to determine the constitution of the acid melting at 267°. As a preliminary step its molecular weight was determined, using alcohol as a solvent.

1.3230 grams of the acid dissolved in 53.63 grams of absolute ethyl alcohol gave a rise of 0.108° in the boiling point (corrected for barometric change) corresponding to a molecular weight of 264.8. Considering this result in connection with the formation of diphenylsulphone by distilling the acid with lime, and also in view of the analyses of the acid and of its salts by Canter, there remained no doubt that the formula of the acid is  $C_6H_4\begin{cases} COOH \\ SO_2.C_6H_5 \end{cases}$, according to which its molecular weight should be 260.18.

If this is the case it is isomeric with phenylsulphoneorthocarbonic acid, which has been proved to be an ortho compound. Plainly, the acid melting at 267° required more careful investigation.

2. Purification of Orthotolylphenylsulphone.

About 40 grams of orthotolylphenylsulphone was prepared as before. In recrystallizing this substance it was found that if more alcohol was used than was necessary for solution, and the crystals which separated first were filtered off and dried, they did not melt at 67.5°-68°, but several degrees higher. This indicated the presence of a hitherto unnoticed impurity in the product which melted at 67.5°-68°. Following up this clue, five or six fractional re-

crystallizations, allowing only a small proportion of the product in solution to separate each time, gave a product which crystallized in beautifully regular, colorless, rhombic plates, which melted sharply at 80°. By this method only a very small quantity of the pure substance was obtained, but by seeding the solution of the lower melting material with small crystalls of the product melting at 80°, a larger quantity of the pure material was obtained. The difficulty of purifying this material is a typical example of the tendency which compounds of this group have to crystallize in mixtures having definite melting points, which remain unaffected by repeated recrystallizations. This particular case is very interesting from the fact that the process can be observed under the magnifying glass. The first crystals which appear from a solution of the substance melting at 67.5°-68° are very small, but are perfectly shaped rhombic plates, which move around in the solution, and rapidly increase in number. After the crystallization has proceeded for a time, however, the points of the diamond shaped crystals become blunt or rounded. The crystals should be quickly filtered off by means of a pump as soon as the slightest sign of this change of form is seen. If this is done very quickly the crystals will be found to be almost entirely pure, melting at very nearly 80°. If the crystallization is allowed to continue, and if the solution is fairly concentrated, the resulting crystals are irregularly shaped leaflets, and melt at 67.5°-68°. This is really rather a sharp softening than a true melting of the substance, however, as the liquid in the melting-point tube is not entirely clear, and does not lose its cloudiness until a temperature of about 71° is reached, but the change is so sudden

and sharp at 67.5°-68° that it can very easily be mistaken for a true melting of the compound. A great number of crystallizations of the substance melting at 67.5°-68° is necessary in order to prepare even a small proportion of the pure material melting at 80°, and by actual experiment three weeks work was required to separate 10 grams of the substance melting at 80° from 40 grams of the substance melting at 67.5°-68°. This is due to the fact that only a very small quantity of the rhombic crystals separate at each crystallization before they have to be filtered off and the process repeated, which makes the separation of the pure material exceedingly tedious. The corrected melting point of this substance is 81°.

A few grams of the substance which melted at 80° were oxidized with potassium permanganate in the manner described above. The product was entirely phenylsulphoneorthocarbonic acid, and the yield was very satisfactory. This shows that the product melting at 80° is the true orthotolylphenylsulphone. Not a trace of the acid melting at 267° was obtained in this experiment, though very careful search was made for it.

From this it was evident that the acid obtained by Canter, which melts at 267° is not formed from the same sulphone that gives phenylsulphoneorthocarbonic acid, but from another isomeric sulphone which is also present in the product as first obtained, melting at 67.5°-68°. Considering the difficulty experienced in freeing orthotoluenesulphone chloride from the paratoluenesulphone chloride which is always formed at the same time and which can only be removed by indirect methods, it seemed probable that the second sulphone might be derived from some paratoluenesulphone chloride which was present

in the supposed pure orthotoluenesulphone chloride which served as a starting point in the preparation of the tolylphenylsulphone which melted at 67.5°-68°.

To test this point the amide was made from the toluenesulphone chloride used by Canter and myself. Crystals melting at 154°-155°, which is the melting point of orthotoluenesulphone amide, were first obtained. From the original ammoniacal filtrate some crystals of orthotoluenesulphone amide also separated. These were filtered off, the filtrate was evaporated to dryness, pulverized, washed on a filter with small portions of cold water, and the slight residue was then dissolved in a little hot water. On cooling, white plates separated which melted at 104° (uncorr.). This melting point is known to be one of the melting points of a mixture of ortho and paratoluenesulphone amides.(1)(2) When pure orthotoluenesulphone amide and pure paratoluenesulphone amide are mixed in equal proportion in hot aqueous solution and allowed to crystallize, the product is a mixture melting generally at 120° or 104°-108°(uncorr.). Intermediate melting points may be obtained, but recrystallization results in separating the product into two portions, one melting at 120° - the other at 104°-105°. From these mixtures neither constituent can be separated in a pure condition.

From this it was evident that the orthotoluenesulphone chloride used by Canter, and also in the present work, was impure, and contained some paratoluenesulphone chloride, and it seemed very

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(1) Ber. d. Chem. Ges. 10, 943.

(2) Amer. Chem. Jour. 1, 170.

probable that the acid obtained by Canter, melting at 267°, was derived, not from orthotoluenesulphone chloride, but from the para compound. The acid in the para series, corresponding to the acid made by Canter, had been made in this laboratory by Newell in 1895, but the melting point which he recorded was 273°, instead of 266°-267°, as given by Canter, or 267°, as herein recorded. Since Newell states that he used a Zincke thermometer this difference is not surprising, as the other determinations were made with long stemmed thermometers. However, to avoid any possible confusion on this point, it was decided to make a specimen of paraphenylsulphonebenzoic acid and test its identity with the acid obtained by Canter by direct comparison.

VI. PARAPHENYLSULPHONEBENZOIC ACID.

This acid, as has been stated elsewhere, was first prepared by Michael and Adair(1) from paratolylphenylsulphone by oxidation with potassium permanganate in acetic acid solution, and also by boiling the sulphone with potassium permanganate dissolved in a large excess of water. The yield was exceedingly small in each case. They give the melting point of the acid as "above 300°".

In 1895 Newell,(2) working in this laboratory, investigated this acid. He prepared it by oxidizing paratolylphenylsulphone by means of chromic acid in glacial acetic acid solution. He found the melting point of the acid to be 273° (uncorr.), using a Zincke thermometer. The acid was now made by a method analogous to that used by Weedon in preparing phenylsulphoneorthocarbonic acid. Paraaminobenzoic acid was converted into paraphenylsulphidebenzoic acid, and

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(1) loc. cit.
(2) loc. cit.

this, by oxidation with potassium permanganate, into paraphenylsulphonebenzoic acid.

1. Paraphenylsulphidebenzoic Acid.

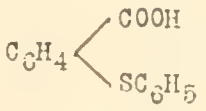
A mixture of 40 grams of paraaminobenzoic acid, 64 cc. of concentrated hydrochloric acid, and 300 cc. of water is cooled to 0° in a thickwalled beaker, surrounded by crushed ice. A concentrated solution of 22 grams of sodium nitrite is added in small portions, with stirring, the temperature being kept below 5° by addition of crushed ice from time to time. After the reaction is complete the diazo solution is run in a thin stream from a dropping funnel into a solution of 34 grams of thiophenol, 60 grams of caustic soda, and 300 cc. of water, which has been heated in a large beaker on a water bath to 50°-60°. During the addition of the diazo solution the mixture must be stirred constantly. A light yellow, curdy precipitate is formed at the point where the diazo solution enters the thiophenolate solution, but this dissolves on stirring, with evolution of gas, forming a dark red solution. After all of the diazo solution has been added the red solution is heated on the water bath until the evolution of gas ceases. After cooling it is acidified with strong hydrochloric acid, and paraphenylsulphidebenzoic acid is precipitated as a dark red mass, which is filtered off by means of a Buchner funnel and suction. The acid is then dissolved in a solution of sodium carbonate and filtered from phenyldisulphide which is formed by the oxidation of a part of the thiophenol. Paraphenylsulphidebenzoic acid is again precipitated by acidifying the filtrate with strong

hydrochloric acid. As thus obtained the acid is very impure, and has the appearance af a red tar, which solidifies on standing. It can not be purified by crystallization from alcohol, glacial acetic acid, ether or benzene, as the tar is about equally as soluble as the acid in these solvents. Neither can the purification be effected by making the barium or calcium salt of the acid. The only method of purification which was to the slightest degree satisfactory was to extract the paraphenylsulphidebenzoic acid by means of boiling ligroin, using a Soxhlet apparatus and continuing the extraction for days, or even weeks. The acid is very difficultly soluble in ligroin, while the tar is practically insoluble. After the extraction is complete the ligroin is distilled off and the acid purified by crystallization from alcohol. It crystallizes in light, colorless, feathery, elongated hexagonal plates, which melt at 173° (uncorr.). The corrected melting point is 177°.

The acid as thus prepared does not contain water of crystallization. Analysis gave the following results:

0.1621 gram gave 0.4012 gram of CO_2 and 0.0625 gram of H_2O.

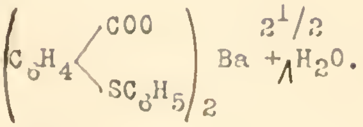
0.2457 gram gave 0.2515 gram $BaSO_4$.

Percentage.	Calculated for  $C_6H_4\left\langle\begin{matrix}COOH\\SC_6H_5\end{matrix}\right.$.	Found.
C	67.82	67.48
H	4.35	4.27
S	13.91	14.02

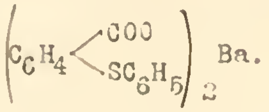
The barium salt of this acid is difficultly soluble in boiling water, from which it crystallizes in very thin plates, containing 2 1/2 molecules of water of crystallization. Analysis gave the fol-

lowing results:

0.1113 gram of air dried salt lost 0.0081 gram H 0 when heated to 140° for 2 hours.

Percentage.	Calculated for  $\left(C_6H_4\begin{smallmatrix}COO\\SC_6H_5\end{smallmatrix}\right)_2Ba + 2\tfrac{1}{2}H_2O$.	Found.
H_2O	7.02	7.27

0.1026 gram of dehydrated salt gave 0.0401 gram $BaSO_4$.

Percentage.	Calculated for  $\left(C_6H_4\begin{smallmatrix}COO\\SC_6H_5\end{smallmatrix}\right)_2Ba$.	Found.
Ba	23.07	22.98

2. Oxidation of Paraphenylsulphidebenzoic Acid by Means of Potassium Permanganate.

When paraphenylsulphidebenzoic acid is heated with a slight excess of potassium permanganate in a large excess of water, paraphenylsulphonebenzoic acid is formed. The method is exactly the same as that already described in the case of oxidizing orthotolylphenylsulphide, but the oxidation is complete in about two hours. The filtrate from the oxides of manganese is acidified, after evaporating to a small volume, while hot. If the solution is cold paraphenylsulphonebenzoic acid is precipitated so finely divided that it is almost impossible to filter it.

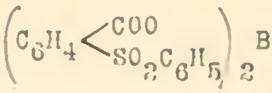
As thus obtained the acid is a fine, crystalline, white powder. It is easily soluble in alcohol, from which it crystallizes in small, white leaflets which melt at 267° (uncorr.). The corrected melting point is 277°. It is insoluble in benzene and water.

A portion of this substance was mixed with an equal portion of the acid melting at 267°, which had been prepared in the manner described by Canter from the crude orthotolylphenylsulphone melting at 67.5°-68°. The melting point of the mixture showed no change. From this there can be no doubt that the acid obtained by Canter, melting at 267°, is really paraphenylsulphonebenzoic acid and not the ortho compound, as he supposed. As has been stated, Newell found the melting point of this acid to be 273° (uncorr.) using a Zincke thermometer.

The salts of this acid as described by Canter, contain much more water of crystallization than they do according to Newell. Newell, however, did not heat the salts to as high a temperature as Canter did. A sufficient quantity of the acid was not at hand during this investigation to permit of a thorough examination of all of the salts made by Canter. The barium and calcium salts were made, however, and from the behavior of these two salts it seems probable that the figures given by Canter are more nearly correct than those given by Newell. Neither of these salts loses water of crystallization to any great extent at 110°, or even at 130°, but at 165° all of the water is easily removed. The salts lose most of their water by standing in a desiccator for several days.

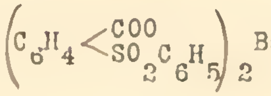
The barium salt crystallizes in slender, white needles, containing three molecules of water of crystallization. Analysis gave the following results:

0.0839 gram air dried salt, heated to 165° for an hour and a half, lost 0.0064 gram H_2O.

Percentage	Calculated for  $\left(C_6H_4<\begin{matrix}COO\\SO_2C_6H_5\end{matrix}\right)_2Ba + 3H_2O$.	Found.
H_2O	7.57	7.63

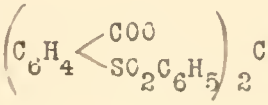
I. 0.1467 gram anhydrous salt gave 0.0517 gram $BaSO_4$.

II. 0.1770 gram anhydrous salt gave 0.0630 gram $BaSO_4$.

Percentage	Calculated for  $\left(C_6H_4<\begin{matrix}COO\\SO_2C_6H_5\end{matrix}\right)_2Ba$.	Found.	
		I.	II.
Ba	20.81	20.79	20.92

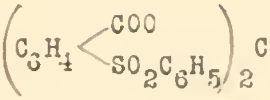
The calcium salt crystallizes in fine, white needles, containing 6 molecules of water of crystallization. Analysis gave results as follows:

0.1817 gram air dried salt, heated to 165° for an hour and a half, lost 0.0294 gram H_2O.

Percentage.	Calculated for  $\left(C_6H_4<\begin{matrix}COO\\SO_2C_6H_5\end{matrix}\right)_2Ca + 6H_2O$	Found.
H_2O	16.14	16.18

I. 0.1525 gram anhydrous salt gave 0.0365 gram $CaSO_4$.

II. 0.1030 gram anhydrous salt gave 0.0247 gram $CaSO_4$.

Percentage.	Calculated for  $\left(C_6H_4<\begin{matrix}COO\\SO_2C_6H_5\end{matrix}\right)_2Ca$.	Found.	
		I.	II.
Ca	7.11	7.04	7.06

Though there now remained no doubt as to the identity of the acid described by Canter, the melting points found by him for the chloride and amide of this acid differ so much from those given by Newell that it was thought necessary to examine these compounds. In the experiments made to determine this question the acid which was used was that which had been prepared by the method of Canter, but

that used in preparing the salts described above, was made by oxidizing paraphenylsulphidebenzoic acid.

3. Chloride of Paraphenylsulphonebenzoic Acid.

The acid was mixed with a little more than equal weight of phosphorus pentachloride in a small flask, which was immersed in a sulphuric acid bath. The temperature of the bath was raised gradually to 200°. No action at all could be detected until a temperature of 125° was reached, and the action did not become at all vigorous until 140° was reached. At this temperature the mass melted and hydrochloric acid was given off freely. According to Canter the reaction begins at ordinary temperature and proceeds rapidly when the flask is heated to 45° on the water bath. After heating at 200° for one hour the flask was removed from the bath and the contents were poured into a porcelain dish. The product solidified to a light brown, crystalline mass. This was powdered and washed with water at 40°, first by decantation, and then on a filter, with suction. By this treatment it became almost white. It was then dried and dissolved in boiling ligroin, in which it is difficultly soluble, and from which it crystallized in small, colorless, square plates. After several recrystallizations the melting point was found to be 143°-144°,(uncorr.). The corrected melting point is 146°-147°. Newell found the melting point to be 145.2° - 145.8°, using a Zincke thermometer. Canter crystallized it from glacial acetic acid and gives its melting point as 262.5°-.263.5°.

4. Amide of Paraphenylsulphonebenzoic Acid.

A portion of the chloride of paraphenylsulphonebenzoic acid, prepared as above, was digested with a large excess of concentrated ammonia for 24 hours at ordinary temperature. The insoluble product was filtered off, washed with cold water and then dissolved in boiling water, in which it is rather difficultly soluble. On cooling, feathery white crystals separated, which melted at 240°-240.5° (uncorr.). The corrected melting point is 248.3°-248.8°. Newell gives 242°-243° using a Zincke thermometer. Canter gives 254°-253° as the melting point.

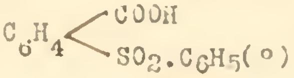
CONCLUSIONS.

The results of this investigation may be summarized as follows:

1. When phenylthiosalicylic acid is oxidized with dilute nitric acid the product of the reaction is almost entirely phenylsulphoxideorthocarbonic acid, as stated by Weedon.

2. When phenylthiosalicylic acid is treated with fuming nitric acid a substance is obtained having the melting point of the acid described by Graebe and Schultess. This substance is a mixture of phenylsulphoxideorthocarbonic acid and a mononitro derivative of this acid. The proportion of the nitro compound is increased by heating the solution of phenylthiosalicylic acid in fuming nitric acid.

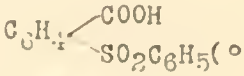
3. When phenylthiosalicylic acid is oxidized by means of potassium permanganate, phenylsulphoneorthocarbonic acid is formed, as stated by Weedon. The reactions of this acid show it to have the formula


$C_6H_4{<}\begin{matrix}COOH\\SO_2.C_6H_5(o)\end{matrix}$

, given by Weedon.

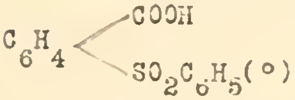
4. When orthotolylphenyl sulphide is oxidized by means of potassium permanganate, phenylsulphoneorthocarbonic acid is formed.

5. The acid melting at 267°, obtained by Canter, and supposed by him to be orthophenylsulphonebenzoic acid,


$C_6H_4{<}\begin{matrix}COOH\\SO_2C_6H_5(o)\end{matrix}$

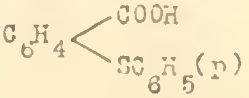
, is really the isomeric paraphenylsulphonebenzoic acid, which had been made previously by Newell. Its formation under the conditions of Canter's investigation was due to the presence of paratoluenesulphone chloride in the orthotoluenesulphone chloride with which he worked.

6. When pure orthotolylphenylsulphone is oxidized with potassium permanganate, phenylsulphoneorthocarbonic acid,


$C_6H_4{<}\begin{matrix}COOH\\SO_2C_6H_5(o)\end{matrix}$

, is the only product obtained.

7. Paraphenylsulphidebenzoic acid is obtained from para-aminobenzoic acid and thiophenol by a process exactly analogous to the preparation of phenylthiosalicylic acid from anthranilic acid and thiophenol. Paraphenylsulphidebenzoic acid is oxidized to paraphenylsulphonebenzoic acid by means of potassium permanganate, just as phenylthiosalicylic acid is oxidized to phenylsulphoneorthocarbonic acid under similar conditions. This reaction, together with analyses of the acid and of its barium salt, show the formula of paraphenylsulphidebenzoic acid to be


$C_6H_4{<}\begin{matrix}COOH\\SC_6H_5(p)\end{matrix}$

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BIOGRAPHICAL.

Howard Waters Doughty was born in Baltimore, Maryland, August 13, 1871. He received his early education in the Friends' Elementary and High School, of Baltimore. In 1889-1890 he studied at the Rensselaer Polytechnic Institute, Troy, N. Y. In October, 1890, he entered the Johns Hopkins University, and devoted the following three years to the study of Electrical Engineering, receiving the title of "Proficient in Electrical Engineering" in 1893. The next seven years were spent in commercial life. In October, 1900, he entered the Johns Hopkins University as a student in chemistry. In 1902-1903 he was University Scholar in chemistry at the University. In 1903-1904 he held a fellowship in chemistry at the University. His subordinate subjects have been Physical Chemistry and Physics.